# Heterogeneously catalysis in an oscillatory baffled flow reactor

Valentine Eze,<sup>b</sup> Anh N Phan,<sup>b</sup> Cyril Pirez,<sup>a</sup> Adam P. Harvey,<sup>b</sup>\* Adam F. Lee<sup>a</sup> and Karen Wilson<sup>a</sup>\*

# **Supplementary Information**

## S1 Experimental section

S1.1 Reactor configuration



Fig. S1 Experimental set-up for batch SBA-SO<sub>3</sub>H catalysed esterification.

Electronic Supplementary Material (ESI) for Catalysis Science & Technology This journal is © The Royal Society of Chemistry 2013



Fig. S2 Residence time distribution of the integral baffled reactor from experimental data using  $(E(\theta) = \tau \frac{C_i}{\sum_i C_i \Delta t_i})$  and the tanks-in-series model  $(E(\theta) = \frac{N(N\theta)^{N-1}}{(N-1)!}e^{-N\theta})$  at a flow rate of

22ml/min under an oscillatory flow.

#### S1.2 Catalyst Synthesis

SBA-15 was prepared following the method of Zhao *et al* [i], using 1.0 g of Pluronic P123 triblock copolymer (Aldrich), which was dissolved in 7.5 ml of water and 25 ml of 2M HCl solution (Fisher) while stirring at 35 °C. 2.3 ml of TEOS (tetraethoxyorthosilane - Aldrich 99%) was then added to the solution, which was maintained at 35 °C for 24 h while stirring. The mixture was then aged statically at 80 °C for a further 24 h in a closed propylene bottle after which the solid product filtered, washed 3 times with deionised water, dried and calcined in air at 550 °C for 6 h. SBA-15 was functionalised with sulfonic acid groups by post-grafting, in which 1 g of SBA-15 was added to a solution containing 1 ml of mercaptopropyl trimethoxysilane (MPTS 95%, Alfa Aesar) in 30 ml of toluene (Fisher 99%). The suspension was then refluxed at 130 °C under stirring for 24 h, after which the resulting thiol-functionalised solid was filtered, washed three times with methanol (Fisher 99%) and dried at 80 °C overnight. Thiol groups were converted into  $-SO_3H$  by mild oxidation with 30 ml of 30 % hydrogen peroxide (Sigma-Aldrich) by continuous stirring at room temperature for 24 h. The sulfonated solid product was subsequently filtered, washed three times with

methanol and dried at 80 °C. Materials were stored in air and used without further modification.

#### S 1.3 Catalyst characterisation

Textural and structural properties were measured by a combination of  $N_2$  porosimetry, TEM and XRD, with pre- and post-oxidation sulfur content determined by TGA (bulk) and XPS (surface), with acid site titrations performed by NH<sub>3</sub> pulse chemisorption.

Nitrogen porosimetry was undertaken on a Quantachrome Nova 1200 porosimeter, with samples degassed at 120 °C for 2 h prior recording adsorption/desorption isotherms. BET surface areas were calculated over the relative pressure range 0.01-0.2, while pore diameters were calculated by applying the BJH method to the desorption branch of the isotherm. Low angle XRD patterns were recorded on a PANalytical X'pertPro diffractometer fitted with an X'celerator detector and Cu Kα (1.54Å) source. Low angle diffraction peaks were recorded over the range  $2\theta = 0.3-8^{\circ}$  with a step size of  $0.01^{\circ}$  and calibrated against a Si standard. TEM images were viewed with a Phillips CM12 transmission electron microscope operating at 100 kV. Images recorded by a SIS MegaView III digital camera, with the data analysed using ImageJ software. SEM/EDX was performed with a Carl Zeiss Evo-40 instrument, with samples mounted on conductive carbon tape. XPS was performed on a Kratos Axis HSi instrument fitted with a charge neutraliser and magnetic focusing lens employing Al Ka monochromated radiation (1486.7 eV). Spectral fitting was performed using CasaXPS version 2.3.14, with binding energies corrected to the C 1s peak at 284.5 eV, with S 2p XP spectra fitted using a common Gaussian/Lorentzian peak shape. Errors were estimated by varying the Shirley background-subtraction procedure across reasonable limits and recalculating the component fits. TGA was performed using a Stanton Redcroft STA780 thermal analyser at 10 °C.min<sup>-1</sup> under flowing He (20 ml.min<sup>-1</sup> total) for hydroxyl group density and sulfonic acid decomposition studies respectively.

Acid site titration was performed on a Quantachrome CHEMBET-3000 instrument by pulse chemisorption, using pure NH<sub>3</sub> (BOC 99.98 %). ~50mg of catalyst was outgassed at 150 °C for 2 h under flowing He, after which NH<sub>3</sub> adsorption was performed at 100 °C to prevent NH<sub>3</sub> physisorption on the silica surface. Titration was performed by injecting 500  $\mu$ L pulses

of  $NH_3$  with a gas syringe until the detector signal in both TCD and mass spectrometer reached a plateau, indicating that the acid sites were saturated.

## S1.4 Analytical conditions for reaction profiling

Approximately 0.2ml samples collected at different interval times during the reactions were stored in a freezer set at -20°C and then analysed thereafter using a 5890 Hewlett Packard Series II gas chromatography (equipped with CP Wax Capillary column, BPX70). Methyl hexanoate and methyl octanoate (with purity 99%) were used as internal standards for the analysis of the methyl esters of the propanoic and hexanoic acids, respectively. For the analysis of the methyl esters of the lauric and palmitic acids, methyl heptadecanoate (99%) was used as an internal standard.

About 10mg/mL of the internal standards were prepared in methanol for analysis of all samples collected at a methanol to acid molar ratio of 30:1. For the reactions carried out with hexanoic acid at methanol to acid molar ratio of 1:1, 2:1 and 6:1, the GC internal standard was prepared in heptane (99.5%). The choice of solvent was to ensure total solubility of the samples.

The acid conversions were obtained from the Eq.1.

$$Conversion = \frac{C_{A0} - C_A}{C_{A0}} = \frac{C_{\cdot}\rho_{mix}}{M_E \cdot C_{A0}}$$
(Eq.1)

Where:

 $C_A$  = concentration of the acid;

C = fractional composition of the methyl ester in the sample;

 $C_{A0}$  = initial acid concentration of species (mol.dm<sup>-3</sup>);

 $\rho_{mix}$  = density of the reacting mixture without catalyst (g.dm<sup>-3</sup>)

 $M_E$  = molecular weight of the methyl ester (g.mol<sup>-1</sup>).

## S2 Results & Discussion

**Table S1:** Physical properties of fresh and spent RSO<sub>3</sub>H-SBA-15 catalyst (full details of XP spectra and adsorption isotherms are published in reference [2])

Catalyst	BET (m²/g)	Vp (cm <sup>3</sup> /g)	W <sub>BJH</sub> (nm)	20 (°)	Plane spacing <sup>a</sup> (nm)	Unit cell parameter (nm)	Wall thickness (nm)	Bulk S content <sup>b</sup> (%)	Surf. S content <sup>c</sup> (%)	S/Si atomic ratio	NH <sub>3</sub> titration <sup>d</sup> (mmol/g)	Density (g/ml)
Fresh RSO3H/SBA-15	705	0.782	5.1	1.06	8.36	9.65	4.6	1.01	0.7	8.0E-03	0.43	0.37
Spent RSO3H/SBA-15									0.92	9.4E-03		

<sup>a</sup>Calculated from d(100) reflection using Bragg's Law, <sup>b</sup>S content from TGA, <sup>c</sup>S content from XPS analysis, <sup>d</sup>Acid site loading from NH<sub>3</sub> pulse titration.

The effect of catalyst loading was investigated under batch conditions in the OBR and reveals good first order behaviour.



**Fig. S3** Effect of SBA-SO<sub>3</sub>H catalyst loading on the esterification of hexanoic acid at 60 °C and 30:1 methanol:acid molar ratio in the OBR under batch operation mode.

**Table S2** below shows the initial rates of hexanoic acid esterification in the OBR as a function of reaction temperature. Data was used to determine the activation barrier for reaction over  $RSO_3H$ -SBA-15.

Temperature (°C)	Molar ratio Methanol:Acid	Initial rate (mmol.h <sup>-1</sup> )
40	1:1	2.3
50	1:1	3.6
60	1:1	6.5
$E_a (kJ.mol^{-1})$	-	45.5

Table S2: Temperature dependence of the initial rate of hexanoic acid esterification

#### References

i. D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, J. Am. Chem. Soc. 1998, 120, 6024-6036.

<sup>2</sup> C. Pirez, J.-M. Caderon, J.-P. Dacquin, A. F. Lee and K. Wilson, ACS Catalysis, 2012, 2, 1607-1614.